MOLECULAR ORBITAL THEORY OF THE MAGNETIC PROPERTIES OF THE TETRAHEDRAL COPPER COMPLEX, Cs_2CuCl_4

R. CHATTERJEE, S. LAHIRY, U. S. GHOSH and S. MITRA

Department of Magnetism,
Indian Association for the Cultivation of Sciences, Jadavpur, Calcutta-32.

It has occurred to us that studies of the magnetic behaviour of tetrahedral complexes of the first transition series elements, which have received very little attention compared to the corresponding octahedral ones, would be of interest. And, in this direction, we have derived the theory of magnetic susceptibility and anisotropy of a tetrahedral Copper (II) complex, Cs_2CuCl_4, on the basis of molecular orbital theory of Van Vleck (1939), Stevens (1953) and Bose *et al* (1960). The X-ray determination of this complex by Helmholz and Kruh (1952), and of Morosin and Lingafelter (1961) indicate that the tetrahedron has a tetragonal distortion along the line joining the middle points of the opposite edges of the tetrahedron.

The $3d^9\ ^2D$ ground state of the free Cu^{2+} ion is split under the cubic field into a lower lying orbital triplet, $^2T_2$ and an upper orbital doublet ^2E separated by 10Dq, since the works of Gorter (1932), Van Vleck (1932) and Ballhausen have shown that the stark pattern for a tetrahedral complex is inverted with respect to an octahedral one. Further, the overall cubic separation is 4/9 times less which makes it necessary to consider the effect of upper orbital doublets through the second order spin-orbit coupling. Now operating on the appropriate orbital states

$$|+> = -\frac{i}{\sqrt{2}}[\,|xz> + i|yz>\,]$$

$$|-> = -\frac{i}{\sqrt{2}}[\,|xz> - i|yz>\,]$$

$$|0> = |xy>$$

following Stevens (1953)
where

$$|yz> = N[d_{yz} + \lambda\tfrac{1}{4}\{(\pi x_4 + \pi x_2 - \pi x_1 - \pi x_3) + \sqrt{3}(\pi y_4 + \pi y_2 - \pi y_1 - \pi y_3)\}]$$

$$|xz> = N[d_{xz} + \lambda\tfrac{1}{2}\{\pi x_1 + \pi x_2 - \pi x_3 - \pi x_4\}]$$

$$|xy> = N[d_{xy} + \lambda\tfrac{1}{4}\{(\pi x_3 + \pi x_2 - \pi x_1 - \pi x_4)\sqrt{3}(\pi y_4 + \pi y_1 - \pi y_2 - \pi y_3)\}]$$

are taken from Wolfsberg and Helmholz (1952) in which N is the normalizing factor and λ is a measure of the amount of mixture of ligand p-orbits with the central Cu^{2+} d-orbits, with the appropriate Hamiltonian

$$H = V_{tetragonal} + u_z s_z + \tfrac{1}{2}(u_+ s_- + u_- s_+)$$

where $u.s$ is the spin-orbit interaction term and for a d-hole u is identical with ζL, we get three kramers doublets and their energies where.

$$<+|u_z|+> = -<-|u_z|-> = \zeta_\parallel$$
$$<+|u_-|0> = -<-|u_+|0> = \sqrt{2}\zeta_\perp$$

and, also

$$<+|L_z|+> = -<-|L_z|-> = k_\parallel$$
$$<+|L_-|0> = -<-|L_+|0> = \sqrt{2}k_\perp$$

Operating on these Kramers doublets with the magnetic perturbation, the expression for ionic susceptibility (K_i, i = $\parallel$ or $\perp$ to the tetragonal axis) has been derived which is a complicated one. The experimental values of susceptibility and anisotropy as measured between 300°K and 90°K could be fitted with the theoretical expression with the parmeters given in the table. The value of Δ is to be changed from 145 to 100 cm^{-1} with temperature which has also been observed with many other octahedral complexes too (Bose *et al* 1960, 1961, 1963). The orbital reduction factor k, which takes into account the effect of the admixture of metal d-orbits with ligand p-orbits and the spin orbit coupling coefficient ξ_i which is to be reduced from the free ion value of 828 cm^{-1}, partake the asymmetry of the ligand field.

TABLE

$\zeta_\parallel$ -800 cm^{-1} $k_\parallel$ 0.97 10Dq 6000 cm^{-1}
$\zeta_\perp$ -550 cm^{-1} $k_\perp$ $.89$ (Pappalardo, 1961)

Temp. °K	Angular parameter	Δcm^{-1}	$(k_\parallel - k_\perp) \times 10^6$	$k \times 10^6$ Mean susc.
300	γ^2 .6487	145	532	1695
	α^2 .3517		(526)	(1680)
200	γ^2 = .6576	120	701	2387
	α^2 = .3382		(699)	(2420)
90	γ^2 = .6745	100	1184	5267
	α^2 = .3268		(1176)	(5321)

Δ = tetragonal field separation of the lowest cubic level $^2T_2$.
The values in parentheses are the experimental values.

Details of the theory and evaluation of the experimental data will be published elsewhere in due course. The authors record their gratitude to Prof. A. Bose, D.Sc., F.N.I. for criticism and a many valuable discussions. Of the authors (S.L.) is grateful to the authorities of this institute for permitting him to work as an honorary worker and (S.M.) is thankful to the C.S.I.R. Govt. of India for the award of a Junior Fellowship.

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